

Acid-yield measurements and product studies of gas phase ozonolysis of ethene and isoprene as a function of humidity

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Non-methane hydrocarbons (NMHCs) form an important trace component of the atmosphere and are of particular environmental interest because of their deleterious effects on air quality, Earth's climate system and their semiochemical roles in ecosystems. NMHCs are also important precursors to the formation of secondary organic aerosol (*e.g.* Kavouras *et al.*, 1999). The ozonolysis reactions of olefins represent an important source of carboxylic acids. Although the gas phase acid concentrations are small, they are thought to be key species in SOA formation as a result of their low volatility (*e.g.* Ma *et al.*, 2009). Despite this, factors controlling acid formation are not well understood. Both field and modelling studies have encountered difficulties in determining sources of the high concentrations of carboxylic acids that are observed in the atmosphere. Ethene and isoprene are the two most abundant biogenic NMHCs in the atmosphere; therefore measuring acid-yields from the ozonolysis of these two compounds is instrumental in understanding the *in situ* production of carboxylic acids in the atmosphere.

Gas-phase ozonolysis experiments were conducted at room temperature to determine formic acid yields as a function of relative humidity (RH) using the integrated EXTreme RAnge chamber-Chemical Ionisation Mass Spectrometry technique, employing RHs studied for the ethene system were < 1, 11, 21, 27, 30 % and formic acid yields of (0.07 ± 0.01) and (0.41 ± 0.07) were determined at < 1 % RH and 30 % RH respectively, showing a strong water dependence. RHs studied for the isoprene system were < 1, 10, 25, 30, 45 % and formic acid yields of (0.07 ± 0.01), (0.1 ± 0.01), (0.15 ± 0.03), (0.17 ± 0.02) and (0.18 ± 0.02) were determined respectively, as shown in figure 1. It has been possible to estimate the ratio of the rate coefficient for the reaction of the Criegee biradical, CH₂OO with water compared with decomposition. This analysis suggests that the rate of reaction with water ranges between 1 × 10⁻¹² – 1 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ and will therefore dominate its loss with respect to bimolecular processes in the atmosphere. Global model integrations suggest that this reaction between CH₂OO and water may dominate the production of HC(O)OH in the atmosphere.

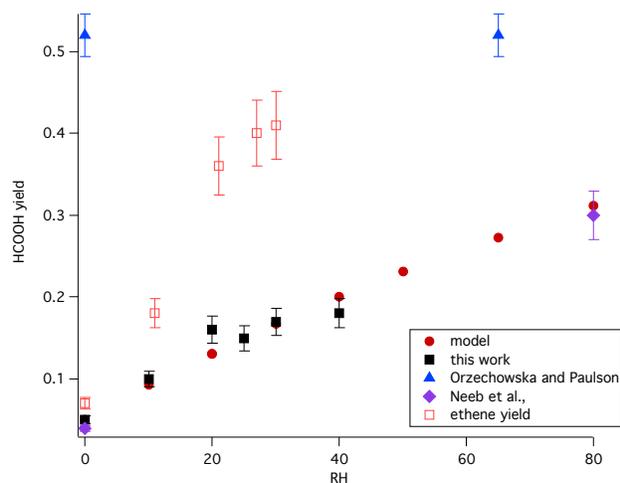


Figure 1 Measured and modelled yields of formic acid from isoprene and ethene ozonolysis

References

- Calvert, *et al.*, *Atmos. Environ.* **1978**, 12, 197.
 Kavouras *et al.*, *Environ. Sci. Technol.* **1999**, 33, 1028.
 Orzechowska *et al.*, *J.Phys. Chem. A* **2005**, 109, 5358.
 Ma *et al.*, *PCCP*, **2009**, 21, 4184.

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